

PORTLAND-ZEOLITE-CEMENT FOR MINIMIZING ALKALI-AGGREGATE EXPANSION

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ABSTRACT

The Authors give an account of the performance modifications induced in the blended cements by replacing the typical pozzolanas with their zeolitic counterparts: volcanic tuffs, after suitable grinding. The advantages of such a replacement in terms of minimization of alkali aggregate expansion and of strengths increase at long ages are discussed, emphasizing also the favourable influence of expansion abatement supplied by a previous thermal treatment of the zeolitic addition. The improved strength progress is interpreted in terms of a higher reactivity of the zeolite minerals in comparison with that of the pozzolanic glass and the expansion abatement in terms of ability to incorporate high alkali amounts showed by the abundant amorphous hydrated silicate.

Introduction

The suitability of minimizing alkalis reaction with some siliceous constituents, sometimes present as impurities in the aggregates for concrete, has recently been the more to the fore in Italy, too, owing to certain concurrent factors. They are substantially: the increased cost of thermal unit, favouring the choice of technologies which cause an alkali rise in the clinker (1); the return of dusts in the kiln, for environmental protection, before their immission to stack, which interferes with alkalis removal; the progressive exhaustion of the quarries better studied from the geo-mineralogical standpoint and the consequent use of less investigated aggregates; the advantage of employing aggregates to be found at hand.

expansion due to the neoformation of an alkaline jellylike silicate can be avoided, as is well known (2), by partial replacement of Portland clinker with suitable active additions, such as: pozzolanas, fly ashes, blastfurnace slag, etc. In order to cut down expansion, without detriment to early ages of strength (3), it is therefore imperative to carefully individuate the type and quantity of active addition.

EXPANSION

As a result of a long and systematic investigation devoted to examining thoroughly manifold aspects of the partial replacement of clinker with the zeolite counterparts of the true pozzolanas: the volcanic tuffs (4), we are able to present a type of "pozzolanic" cement prepared by partial replacement of clinker with those tuffs, which is definitely suitable for remarkably reducing or indeed removing, if manufactured with thermal activated zeolitic tuffs, the harmful expansion even with high alkali clinkers (5). The manufacture and technical performance of such a cement are described in detail in the following paper.

Experimental

The tuffs, collected in various National eruptive districts and different geological areas, and content of zeolite minerals diffused in their matrix, have been carefully selected, after suitable grinding, for partial replacement of Portland clinker. The chemical composition of the products used is reported in Tab.1. Pozzolanas n. 4 (leucitic type) and n. 6 (alkali-trachytic type) are the vitreous counterparts of Roman tuffs n. 1 and 3 (low and high Latium) and Neapolitan tuff n. 5, respectively. Zeolite minerals amount has been calculated on the basis of water content. A detailed account of the mineralogical composition and characterization of the above mentioned tuffs is reported in previous papers (6), (7), (8), (9).

Normal gypsum has been added to a clinker (Tab. 1) having $395 \text{ m}^2/\text{kg}$ Blaine surface area. The additions have been in turn ground until a $13 \pm 4\%$ residue on a $32 \mu\text{m}$ sieve. Then blended cements have been manufactured in laboratory by mixing the clinker with 10, 20, 40% of each addition, as it is followed by one hour's thermal activation treatment (1) at 500°C .

It has been ascertained, by means of the pozzolanicity test according to Italian standards (10), that all the blended cements prepared definitely belong to the pozzolanic type when clinker replacement exceeds 10%, the tests here mentioned have been performed.

The results emphasize the influence of each addition, thermally activated or not, on the workability of fresh mix, determined as resistance to the flow of a mortar, according to ASTM C 230-80 Specification. The graphic design of the tests obtained indicates that moderate clinker replacements most of all increase the mixes workability, which, however, definitely decreases as replacement increases. It is to be noticed also that zeolitic additions lower the workability in a slightly higher way than the vitreous counterparts and that the workability goes slightly down again if the addition has been previously activated.

TAB. 1

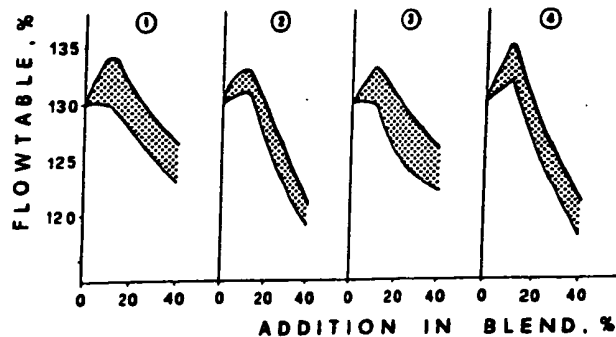
Chemical composition of the active additions (weight %)

Sample number	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	1.0.1.	zeolite type and content
1 tuff	42.0	15.9	9.0	13.0	4.0	0.5	5.4	10.1	chabazite+phillipsite 60%
2 pozzolan	43.3	17.4	9.0	13.4	3.9	0.5	5.9	6.5	-----
3 tuff	50.1	18.7	4.6	5.2	1.2	1.1	5.9	13.5	chabazite 50%
4 pozzolan	54.1	20.9	4.7	4.4	1.5	2.3	6.2	5.8	-----
5 tuff	54.6	17.7	4.1	3.6	0.9	3.4	6.3	9.1	phillipsite 80%
6 pozzolan	57.0	18.3	4.5	3.1	0.9	4.1	8.0	3.7	-----

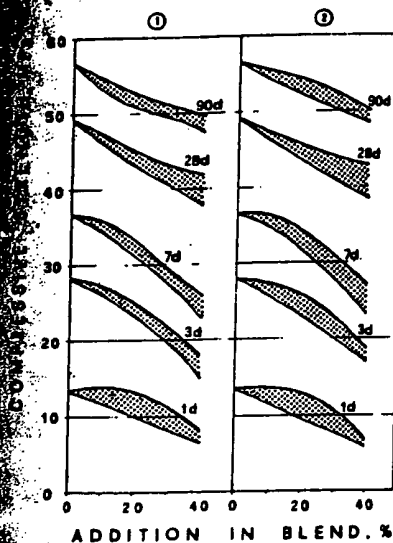
Clinker chemical and potential phase composition

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	SO ₃	Na ₂ O eq.
21.3	3.6	4.5	65.3	1.0	0.7	1.7	2.1	1.8

C₃S = 63%; C₂S = 13%; C₄AP = 14%; C₃A = 2%.



Variation bands of flow values as a function of per cent addition. Mortars manufactured with blended cement containing: (1) pozzolanas, (2) activated pozzolanas, (3) tuffs, (4) activated tuffs.



Variation bands of compressive strength values as a function of per cent addition and curing period. Mortars manufactured with blended cements containing: (1) pozzolanas, (2) activated pozzolanas.

Fig. 2 and 3 answer for the results of the compressive strength tests on standard mortars (11) manufactured with pozzolan- and with tuff-cement samples. The graphic design of the data obtained, as a function of addition amount (activated or not) and curing period, emphasizes the favourable influence of the zeolitic addition in terms of mitigation on the long ages strength decrease, too. It is to be noted also that activation treatment of any type of addition does not effect very much compressive strength of the mortars.

Fig. 4 reports the results of potential alkali reactivity, performed on mortar

prepared using Pyrex glass as aggregate, according to ASTM C 441-81 Specification. Data after six months curing show the remarkable influence of the zeolitic addition on expansion abatement. Such a positive influence is increased the more if the zeolitic addition has been thermally activated. After activation, the zeolitic addition in suitable amount in practice removes the expansion, in comparison with the Portland cement, whereas

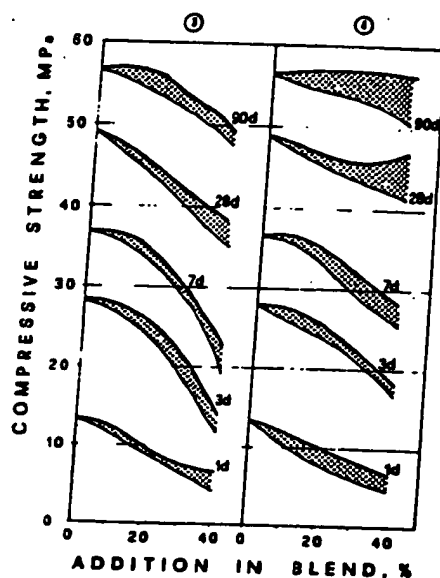


Fig. 3. Variation bands of compressive strength values as a function of per cent addition and curing period. Mortars manufactured with blended cements containing: (3) tuffs, (4) activated tuffs.

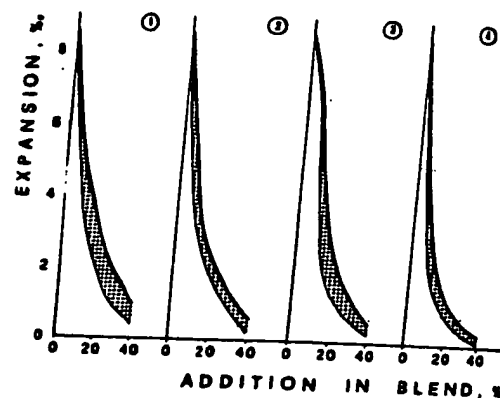


Fig. 4. Variation bands of expansion values as a function of per cent addition. Mortar bars manufactured with blended cements containing: (1) pozzolanas, (2) activated pozzolanas, (3) tuffs, (4) activated tuffs.

the same results can be reached adding a remarkably higher amount of vitreous counterparts.

Discussion and Conclusion

The whole of the experimental results indicate that the partial replacement of clinker with zeolitic additions allows the preparation of blended cements with technical performance better than that of the typical pozzolanic cements manufactured with the vitreous counterparts. Such an improved performance appears in terms both of compressive strength and of minimization of alkali aggregate expansion. Expansion appears moreover the lower if the zeolitic addition has been previously activated by one hour's thermal treatment at 500°C, whilst there is no evidence of such a further abatement after the same treatment of the vitreous counterparts.

At this point it is to be noted that the advantage related to the physical state of the typical incoherent pozzolanas, in comparison to the lithic zeolitic counterparts, is more apparent than effective, since energy consumption for grinding operation does not differ very much for both the products, owing to the peculiar fine-grained texture of the zeolitic tuffs (7). The grinding

PORTLAND CEMENT, ZEOLITES, ALKALI-SILICA REACTION, MINIMUM

of the two products demands in fact about 8-10 Kwh/ton, in comparison with 30 Kwh/ton requested by the clinker, and the drying operation of a tuff, demands 200-250 Kcal/kg.

The decrease of workability induced in the mixes by the zeolitic nature of the addition and the related higher water amount requested, does not influence the mechanical performance. Workability, in any case, can be suitably improved by means of water reducing agents.

Zeolite and phillipsite, representing the main zeolitic minerals to be found, in the amounts, in the matrix of Italian volcanic tuffs, are definitely suitable as active additions to Portland clinker.

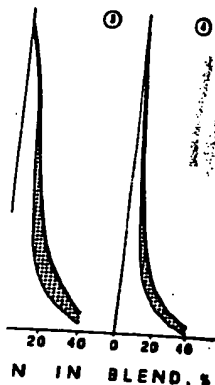
The presence of alkali reactive aggregates, zeolitic additions allow the use of clinkers with alkali content highly exceeding the Na_2O eq. limit of ASTM Specification, according with the advancement of production techniques.

The increase of compressive strength, as well as the increased aptitude for expansion due to alkali aggregate reaction, are both to be interpreted on the basis of a higher reactivity of the zeolite products towards comparison with that of the vitreous counterparts. Owing to the peculiar crystalline structure of porous solids exhibited by zeolite minerals, the specific surface area wider than that of the bubbly pozzolanic glass is subjected to the attack of alkaline solution, so favouring a more rapid and complete formation of the hydrated phases. A more rapid and complete Si-O-Ca bond break, as a consequence of the attack of lime solution, causes, in the neoformation of abundant, low basic, amorphous hydrated calcium hydroxide, which, favouring a more rapid compressive strength progress, can, at the same time, incorporate remarkable alkalis amount, that otherwise would be unavailable for fostering the dangerous expansion reaction.

The further expansion abatement supplied by thermal activation of the zeolitic products can in turn be interpreted on the basis of the following concurrent phenomena: the formation of free bonds at the surface of the solid, owing to the evolution from its pores and channels; a sort of mobilization of the alkali species due to the collapse of the crystalline structure; the wide specific surface area induced in the neoformed amorphous system by the originary crystalline structure of the porous solid.

References

- Sersale and G. Frigione, *Chim. Industr.* **67** (10), 537-541 (1985).
- Hobbs, *Magaz. of Concrete Res.*, **34** (119), 83-94 (1982).
- Sersale in: S.N. Ghosh (ed.), *Advances in Cement Technology*, pp. 537-550, Pergamon Press (1983).
- Sersale and G. Frigione, 7th Int. Conference on Alkali-Aggregate Reaction, Ottawa (Canada) (1986).
- Sersale, *Rend. Soc. Miner. Ital.*, **17**, 499-536 (1961).
- Sersale and G. Frigione, *Chim. Industr.*, **65** (7-8), 479-481 (1983).
- Sersale and G. Frigione, *It. Pat.* 49221 (1983).
- Sersale and G. Frigione, *It. Pat.* 49061 (1984).
- Sersale and G. Frigione, *Chim. Industr.*, **67** (4), 177-180 (1985).



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6. R. Sersale, *Rend. Acc. Sc. Fis. e Mat., Napoli*, 26, 110-116 (1959).
7. R. Sersale, *Rend. Acc. Sc. Fis. e Mat., Napoli*, 27, 306-319 (1960).
8. R. Sersale, *Rend. Acc. Sc. Fis. e Mat., Napoli*, 25, 5-31 (1958).
9. R. Sersale in: L.B. Sand and Mumpton (ed.) *Natural Zeolites. Occurrence, Properties, Use*, pp. 285-302, Pergamon Press 1978.
10. N. Pratini, *Ann. Chim.*, 40, 461-469 (1950).
11. ISO Recommendation R. 679 (1968).

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